

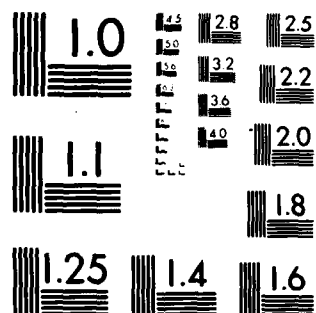
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PROPELLANTS EXPOSIVES AND ROCKET MOTOR ESTABLISHMENT --ETC F/G 7/4  
A CHEMILUMINESCENCE STUDY OF OXIDES OF NITROGEN EVOLVED FROM PR--ETC(U)  
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PROPELLANTS, EXPLOSIVES AND ROCKET MOTOR ESTABLISHMENT  
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6 A CHEMILUMINESCENCE STUDY OF OXIDES OF NITROGEN  
EVOLVED FROM PROPELLANTS.

by

10 I. G. Wallace  
R. J. Powell  
B. J. Downes

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SUMMARY

A chemiluminescence  $\text{NO}_x$  analyser has been used to study nitrogen oxides evolution from single-base and double-base propellants as well as from their nitrate ester ingredients. The technique has illustrated the importance of total oxides of nitrogen as a means of determining the rate at which these materials decompose. The potential of the method as a rapid and unambiguous means of assessing factors such as stability and compatibility is shown. The high sensitivity of chemiluminescence has also permitted the examination of the effect of temperature on decomposition rate down to ambient levels. Consequently one is able to identify changes in the decomposition mechanism as one goes from normal storage temperatures to elevated test temperatures.

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#### FOREWORD

The text of this report was presented as a paper at the 5th Symposium on Chemical Problems Related to the Stability of Explosives, Båstad, Sweden, May 1979.

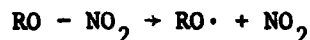
## 1 INTRODUCTION

In the last ten to fifteen years concern over nitrogen oxides as air pollutants has led to the development of analytical instrumentation capable of measuring very low concentrations (sub parts per billion) of these gases. One of the most successful of the instruments has been the Chemiluminescence  $\text{NO}_x$  Analyser.

The object of the present study is to investigate how such an instrument can be used to study some aspects of propellant decomposition.

## 2 PRODUCTION OF OXIDES OF NITROGEN FROM PROPELLANT

Many of the traditional heat and stability tests for nitrate ester based propellants determine in some way the evolution of oxides of nitrogen. This is hardly surprising since the principal mode of decomposition of the nitrate ester is by the familiar reaction



Both the radical and the nitrogen dioxide produced by this initial step undergo further reactions which lead to the production of a number of gaseous products including nitric oxide.

## 3 TRADITIONAL STABILITY TESTS

It is the presence of nitrogen oxides in the product gases from propellant decomposition which forms the basis for most of the traditional stability tests. These tests come in three main types.

3.1 In this group of tests the quantity of gas, produced after heating the propellant for a specified time, is measured and, if the quantity is considered excessive, the material is deemed unstable. Examples of this type of test are:

(a) Will Test: In this test a sample is heated to  $135^\circ\text{C}$  in a stream of  $\text{CO}_2$ . The evolved gases are passed through a mixture of copper and copper oxide where the nitrogen oxides are converted to nitrogen. The carbon dioxide carrier gas is removed by absorption in caustic potash and the volume of the remaining nitrogen is then measured.

(b) Bergman and Junk Test: This is similar to the Will test in that a sample is heated to  $132^{\circ}\text{C}$ . The evolved gases in this case are bubbled through water where nitrogen oxides are dissolved. The acidic contents of the trap are titrated, the result being used to calculate the amount of nitrogen evolved.

3.2 One other approach to stability testing is to measure the time taken to evolve a known quantity of nitrogen oxides. This is the basis of the heat tests which include

(c) Abel Heat Test: Samples are heated at various temperatures in a closed tube which contains a small rectangle of starch iodide paper. Nitrogen dioxide evolved from the propellant reacts with the paper to release iodine which in turn produces a colouration on the paper. The time taken to produce a standard colour is measured and if the time is less than the prescribed time the sample is said to be unstable.

(d) Methyl Violet Test: This is performed in the same way as the Abel test but in this case the test papers containing methyl violet instead of starch iodide are used.

(e) Silvered Vessel Test: Nitrogen dioxide evolution also forms the basis for this test in which the time taken for the heated sample to release sufficient for its characteristic brown colour to be visible. Short fuming times are considered an indication of instability.

3.3 A number of other tests measure nitrogen oxide evolutions by less direct methods. These tests are based on measurement of the amount of stabiliser consumed by reactions with nitrogen oxides. Generally samples are heated at elevated temperatures for prolonged periods after which the residual stabiliser content is measured. Typical of these tests are:

(f) Woolwich Test: The sample is heated at  $80^{\circ}\text{C}$  in a humid atmosphere for 3 weeks after which the stabiliser content is measured. If the level has fallen below a specified proportion of the original the sample is deemed to have failed.

(g) Stanag 4117 Tests: Heating is carried out at  $65.5^{\circ}\text{C}$  for 60 days and the life expectancy of the propellant is estimated from the stabiliser remaining.

These tests show a number of deficiencies:

(i) Some are specific for nitrogen dioxide but show no response to nitric oxide. The Abel and Methyl Violet heat tests fall into this category.

(ii) Either high temperatures and or long times are required to evolve sufficient gas to be measured. Most of the tests discussed suffer this criticism.

The philosophy behind these tests is fairly sound in that by measuring the rate at which oxides of nitrogen are evolved one can estimate the rate at which the propellant is decomposing. There are clearly advantages to be gained therefore in a system which measures the evolution of oxides of nitrogen at low concentrations and eliminates the need for long test times and very high temperatures.

#### 4 THE CHEMILUMINESCENCE NO<sub>x</sub> ANALYSER

Chemiluminescence is a sensitive and specific technique for the determination of nitric oxide. The arrangement of a chemiluminescence instrument is shown in Fig 1.

### CHEMILUMINESCENCE NO<sub>x</sub> ANALYSER

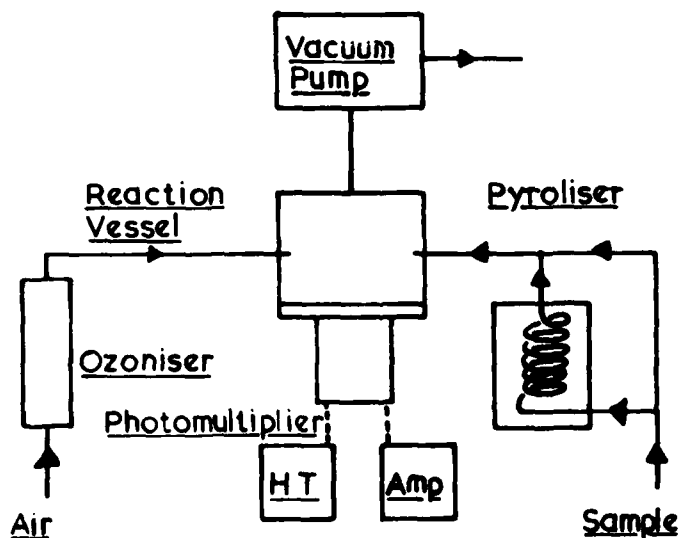
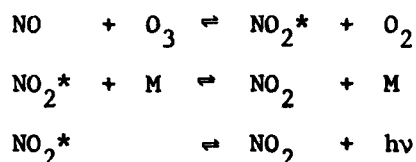


Fig 1

The central feature of a typical analyser is the reaction vessel which is maintained at a reduced pressure. Air is passed through a high voltage ozoniser and the ozone/air mixture produced fed to the reaction vessel where it mixes with sample gas. Any nitric oxide present reacts with the ozone to form excited nitrogen dioxide which on returning to its ground state emits visible radiation.



The intensity of the emitted light is proportional to the nitric oxide concentration and is measured by a photomultiplier and its associated circuitry. The final signal appearing on a recording device is read in parts per million NO.

In order to determine nitrogen dioxide concentration the sample stream is diverted through a heated catalytic converter where any nitrogen dioxide is reduced to nitric oxide which is then determined in the usual way. In this mode of operation nitric oxide is unaffected by the converter. Consequently the reading obtained is sum of nitric oxide and nitrogen dioxide, ie  $\text{NO}_x$ . Nitrogen dioxide is therefore calculated by the difference of the readings obtained in the two different modes of operation ie

$$[\text{NO}_2] = [\text{NO}_x] - [\text{NO}]$$

The capability of the instrument can be best illustrated by a typical specification.

#### Chemiluminescence Specification

Minimum Detectable	=	1 part per billion (ppb)
Range	=	1 ppb to 0.1%
Linearity	=	± 1%
Noise	=	< 1% pp
Precision	=	± 0.5% full scale
Stability	=	± 1% in 24 h
Minimum Sample Flow	=	50 ml/min

## 5 SCOPE OF THE STUDY

The investigations carried out were primarily designed to determine in what areas of propellant technology the chemiluminescence technique might be of value. The experiments carried out were therefore qualitative rather than quantitative in nature.

The study was limited to nitrate ester double-base propellants stabilised with 2-nitrodiphenylamine. The composition of these propellants is summarised in Table 1.

TABLE 1

Propellant	DB 1	DB 2	DB 3
NC	53.0	48.1	) 93.5
NG	42.2	43.3	
DBP	2.8	1.0	6.0
2-NDPA	2.0	2.0	0.5
Ballistic Modifier	3.0	5.6	-

## 6 APPLICATION OF THE TECHNIQUE TO HEAT TESTS

The Abel Heat Test still forms part of the specification for propellants and their nitrate ester ingredients in the UK. For this reason a short study was undertaken to determine how meaningful this test was in terms of its decomposition characteristics.

Apparatus: The apparatus consisted of a modified heat test tube Fig 2.

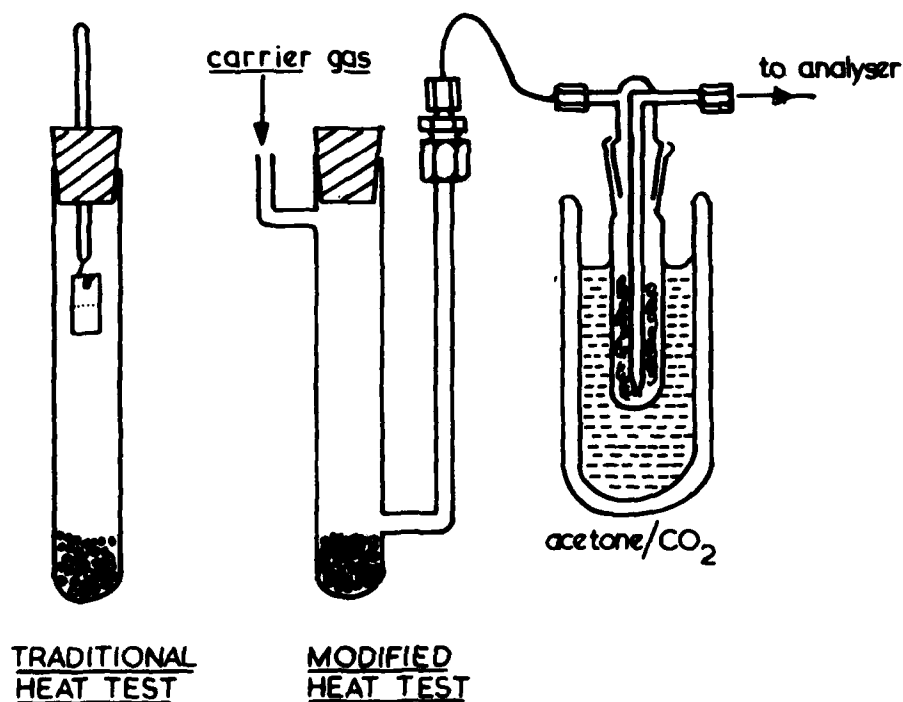


Fig 2

Air was drawn through the tube over the surface of the sample. A trap maintained at  $-80^{\circ}\text{C}$  was used to condense volatile organics and water vapour evolved from the sample. Tests carried out with mixtures of oxides of nitrogen in air confirmed that no loss occurred through the sample train. While the chemiluminescence sample was being run a parallel sample was run using the traditional heat test apparatus to determine if any correlation existed between the two systems.

Results: A typical oxides of nitrogen evolution profile determined by chemiluminescence is shown in Fig 3.

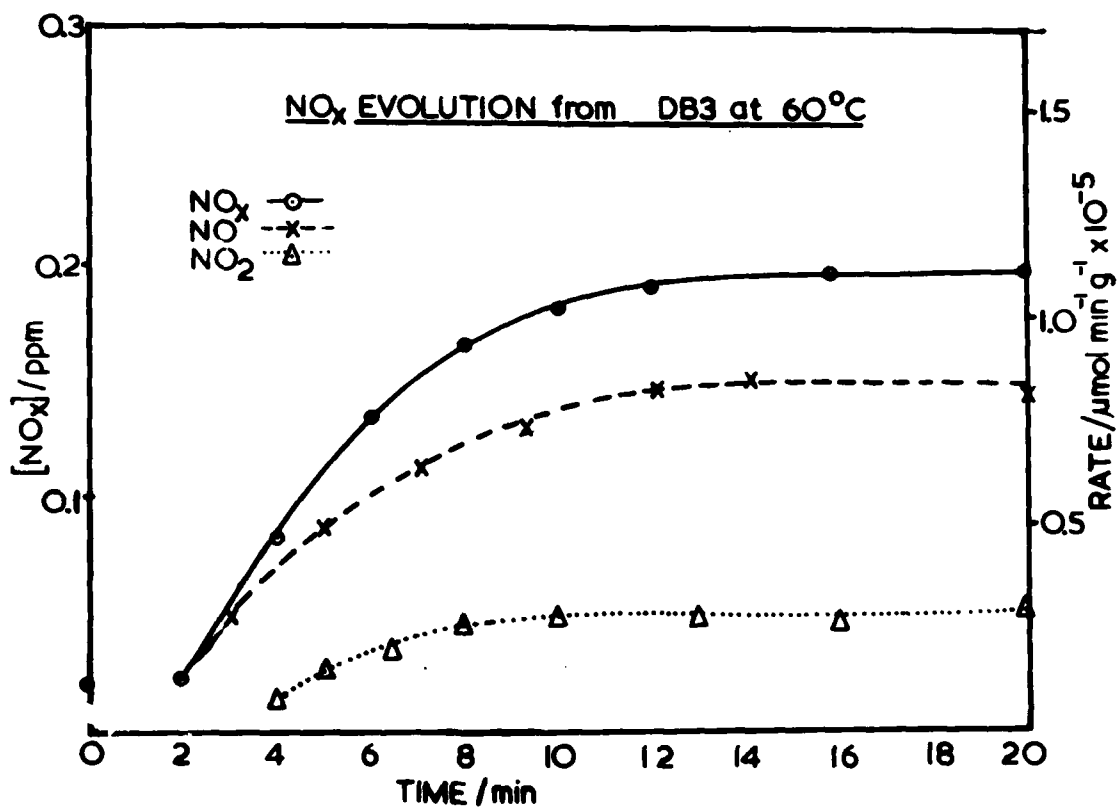


Fig 3

After the sample is placed on the bath, at time ( $t = 0$ ), the concentration of NO<sub>x</sub> can be seen to rise for about ten to fifteen minutes and thereafter it remains constant. The result for samples run for many hours confirms that the evolution rate remains unchanged. Consequently most of the results presented will simply express this constant evolution rate and ignore the initial rise which presumably indicates that the system needs this interval to reach equilibrium. The axes on Fig 3 show both the concentration in parts per million and since the carrier gas flow rate is known, in  $\mu\text{mol min}^{-1} \text{g}^{-1}$  propellant.

The nitrogen dioxide ( $\text{NO}_2$ ) evolution characteristics of a number of different propellants and ingredients is shown in Fig 4. In this case each of the samples was heated at its appropriate heat test temperature.

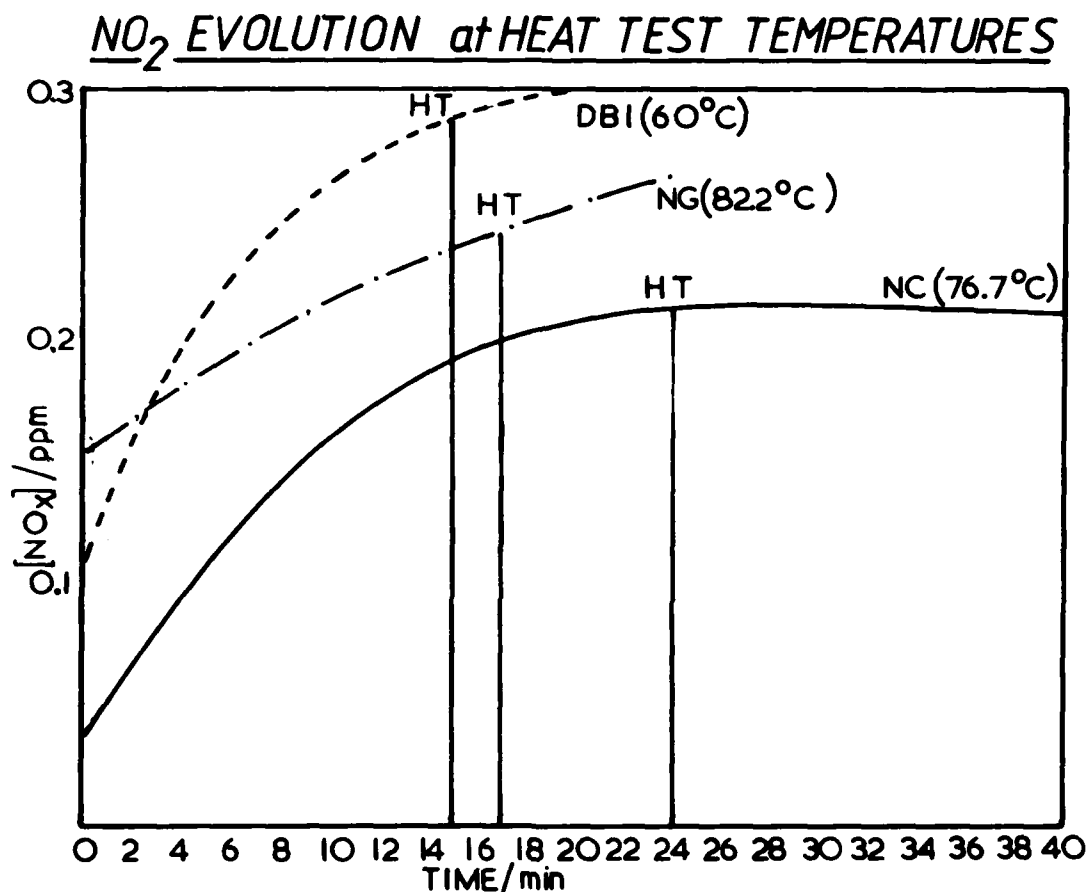


Fig 4

All of the samples show evolution rates of the same order of magnitude. By integrating these rates between  $t = 0$  and the heat test time, it is found that the quantity of nitrogen dioxide required to produce the standard tint is roughly the same for each of the samples.

In contrast to the nitrogen dioxide profiles the  $\text{NO}_x$  evolution characteristics of the same samples are quite different. Fig 5 shows the results of samples run at their Heat Test temperatures.

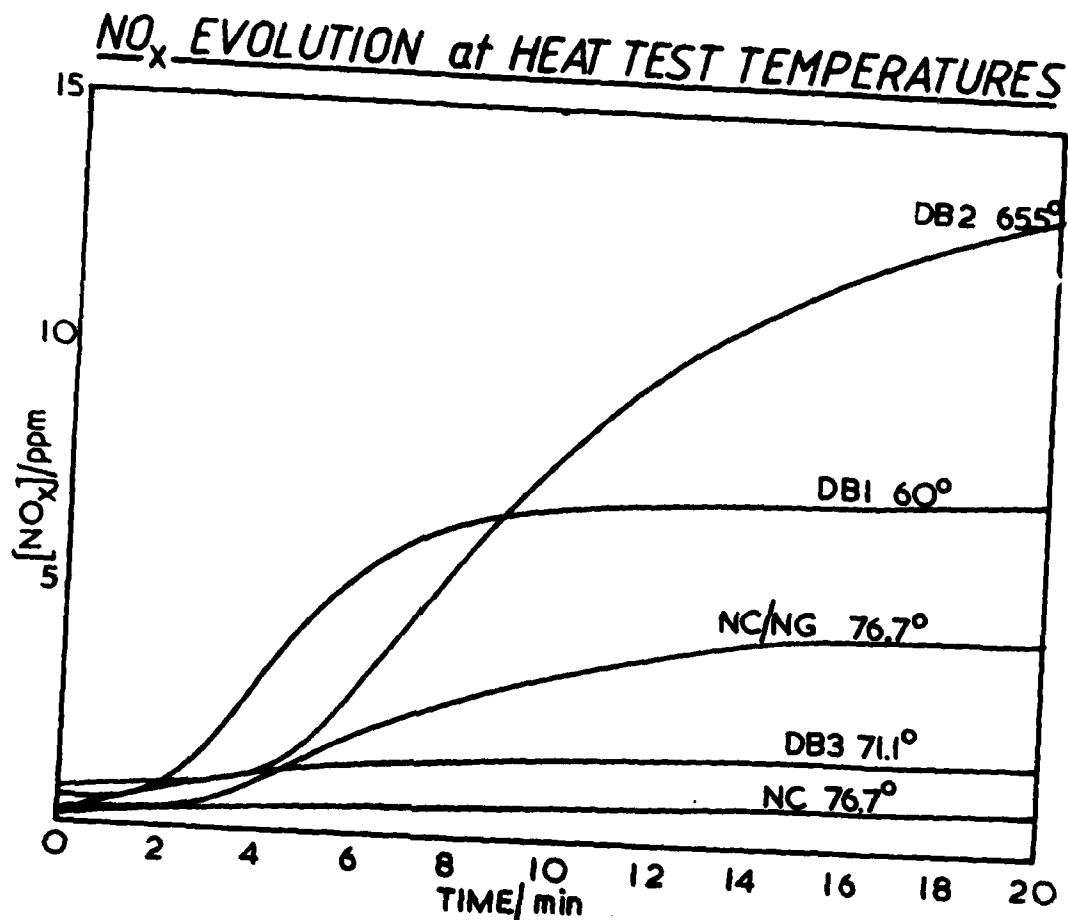


Fig 5

Conclusion: These results suggest that the rate at which a nitrate ester mixture decomposes would appear to be best illustrated by the  $\text{NO}_x$  evolution profile. Although nitric oxide is not a primary decomposition product its only possible mode of formation is by cleavage of an  $\text{RO-NO}_2$  bond followed by reduction of the nitrogen dioxide.

The use of nitrogen dioxide evolution rates, as in the heat test, as a measure of the degree of propellant decomposition would appear to be highly misleading. In the case of double-base propellants, this would underestimate the rate at which nitrate ester  $\text{RO-NO}_2$  linkages are being broken.

In order to characterise the evolution properties of a propellant more realistically it would seem worthwhile to standardise the sample weights and test temperatures. The results shown in Fig 6 were obtained at  $60^\circ\text{C}$  using 1 gram of material as a chosen standard.

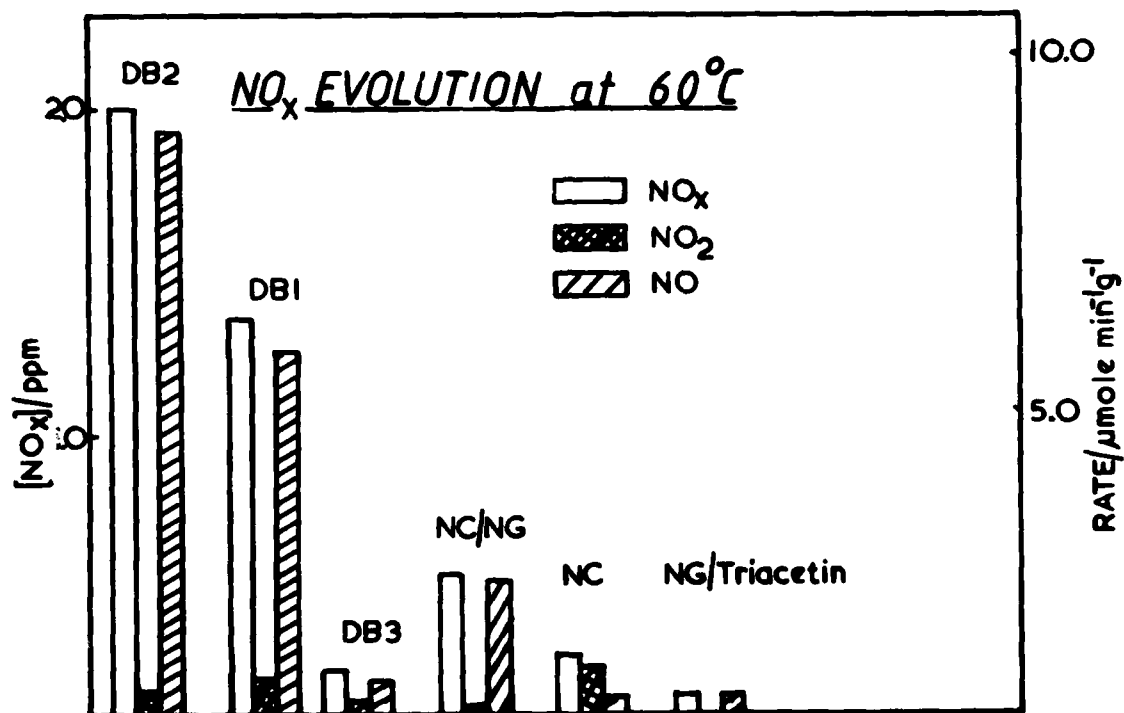


Fig 6

It is believed that these results show the intrinsic decomposition characteristics of the propellant.

7 THE EXAMINATION OF AGED AND UNAGED PROPELLANTS

$\text{NO}_x$  evolution rates have been seen to be different for different compositions of propellant. It is therefore of interest to examine what effect if any "ageing" has on  $\text{NO}_x$  evolution.

Samples examined in this context covered a range of ages from nought to twenty-one years. The constant rates of  $\text{NO}_x$  evolution attained when the samples were heated to  $60^\circ\text{C}$  in the modified heat test tube are shown in Fig 7. The ages and quantity of stabiliser consumed is also reported.

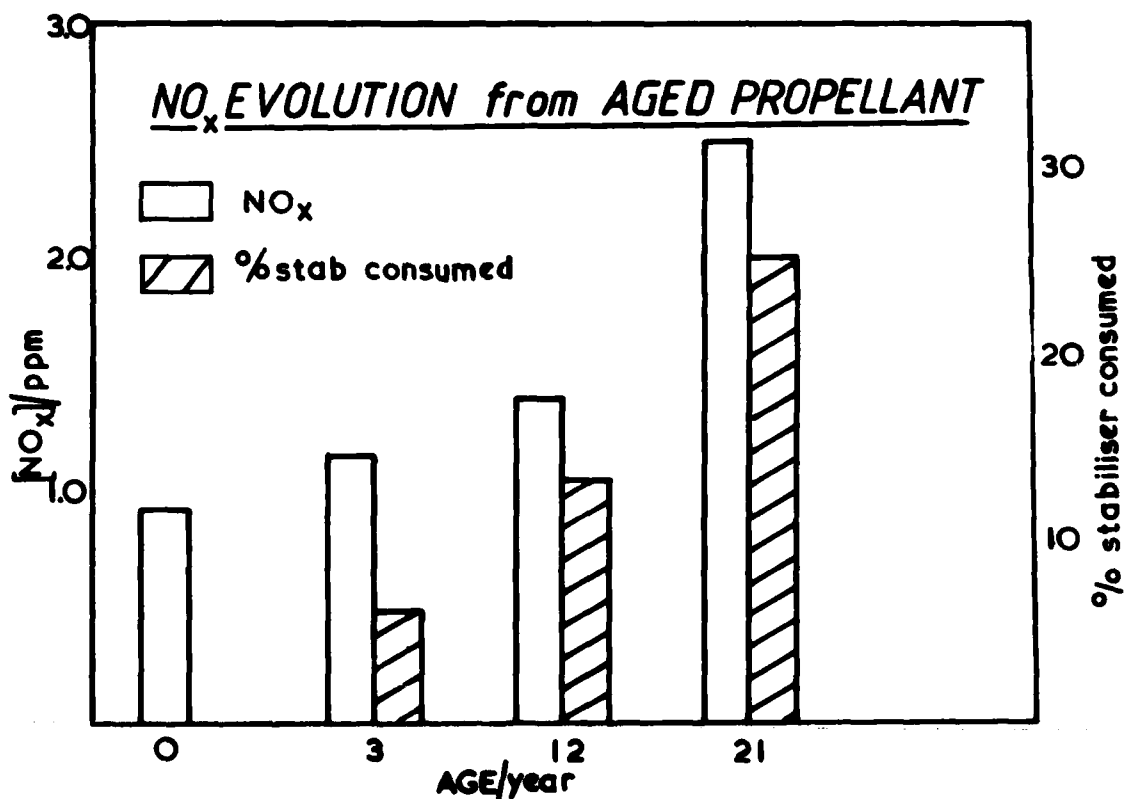


Fig 7

These results show an increase in  $\text{NO}_x$  evolution rate as the age of the propellant increases. At the same time a crude correlation exists between the amount of stabiliser consumed and the evolution rate. Many more experiments will have to be carried out before this or any other correlation can be firmly established. However the indication is that the technique may have a role to play in surveillance of propellants.

## 8 COMPATIBILITY STUDIES

The purpose of compatibility testing is to determine the effect on a propellant or explosive of another material with which it might come into contact.

Experiments were carried out for the purpose of determining what effect a second material had on the rate at which a propellant evolved  $\text{NO}_x$ . In all but one case 1 g was heated at  $60^\circ\text{C}$  with 1 g of a second material in the modified tube. The exception to this procedure was that adopted for a sample of Petrolatum grease as a second ingredient. In this case the grease was coated on glass helices to a loading of 5% and 1 g of these coated helices was mixed with the propellant. It was felt that maintenance of the granular character of the mixture was important from the point of view of comparisons made with other compatibility mixtures.

Results: The results obtained in the compatibility tests are shown in Fig 8 together with results obtained in the traditional vacuum stability tests.

## COMPATIBILITY with DBI at 60°C

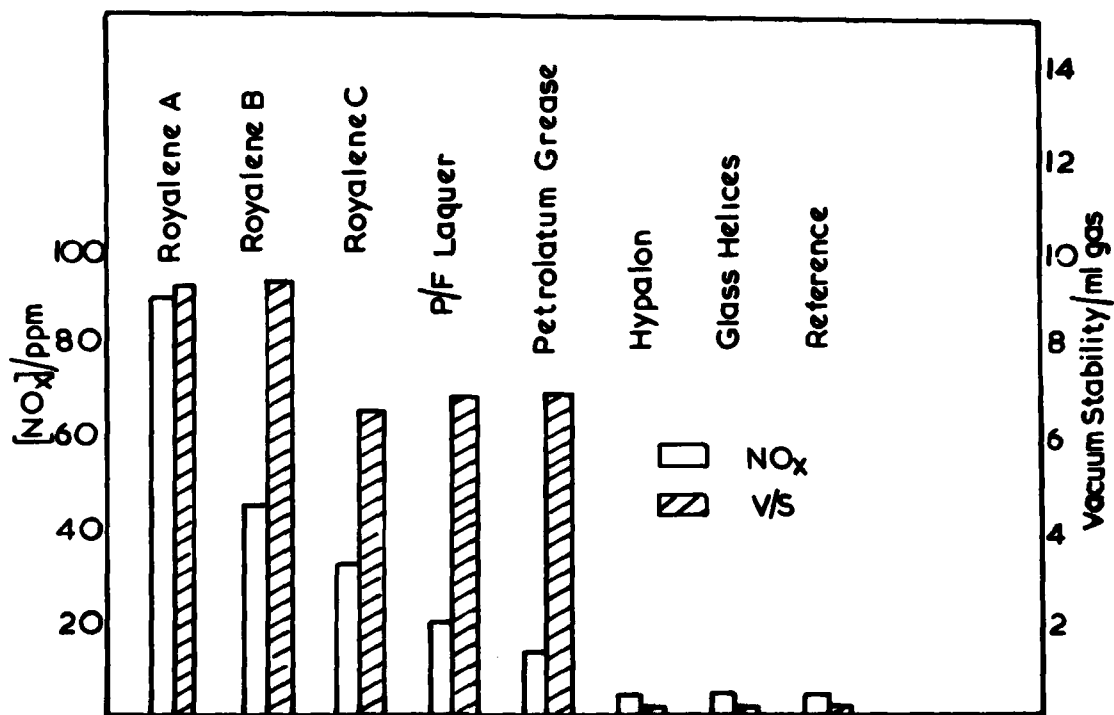


Fig 8

The results show an increase in rate of  $\text{NO}_x$  evolution over that obtained with the propellant on its own. The one exception to this pattern was that obtained with Hypalon rubber which evolved  $\text{NO}_x$  at the same rate as the propellant on its own. These results agree quantitatively with those obtained by the vacuum stability test, where in all cases with the exception of Hypalon an enhanced gassing rate was observed.

**Conclusions:** The chemiluminescence method for examining compatibility problems would appear to offer a number of advantages over the vacuum stability method. The first of these is that a result can be obtained in only a few minutes with only the minimum of sample preparation. The second advantage is that the

result truly reflects an increase in nitrate ester decomposition and not gas producing reactions resulting from the interaction of the materials.

## 9 DECOMPOSITION KINETICS

An experiment was carried out to illustrate the way in which the chemiluminescence technique can be used to study the kinetics of nitrate ester decomposition.

A mixture containing 75% NG, 25% triacetin stabilised with 0.1% 2-NDPA was heated over a range of temperature using the apparatus shown in Fig 9.

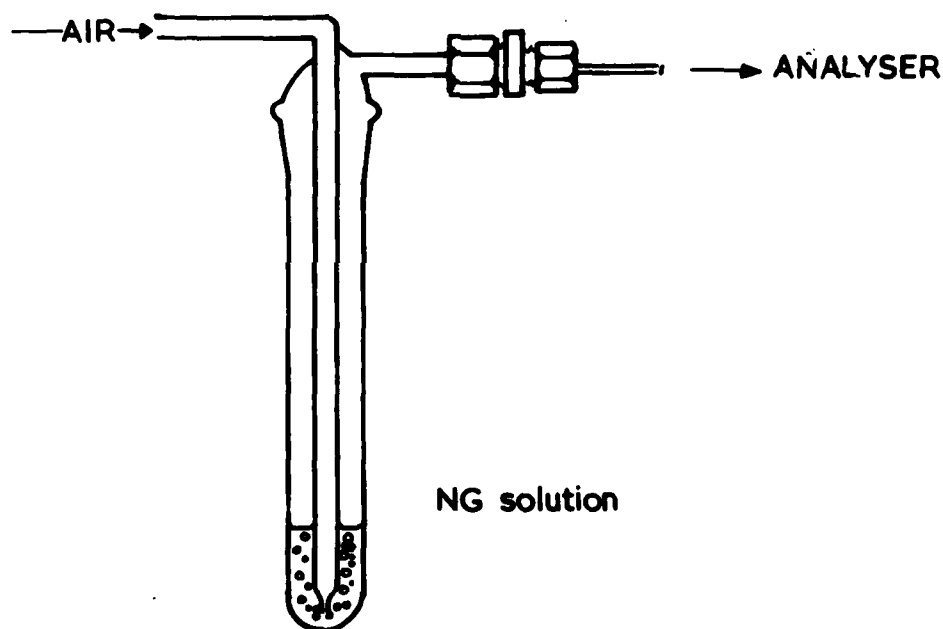


Fig 9

The evolved gases were passed through a cold trap in the usual way and transferred to the analyser. The  $\text{NO}_x$  evolution rate was measured at a number of temperatures between 50 and 95°C. The Arrhenius plot constructed is shown in Fig 10.

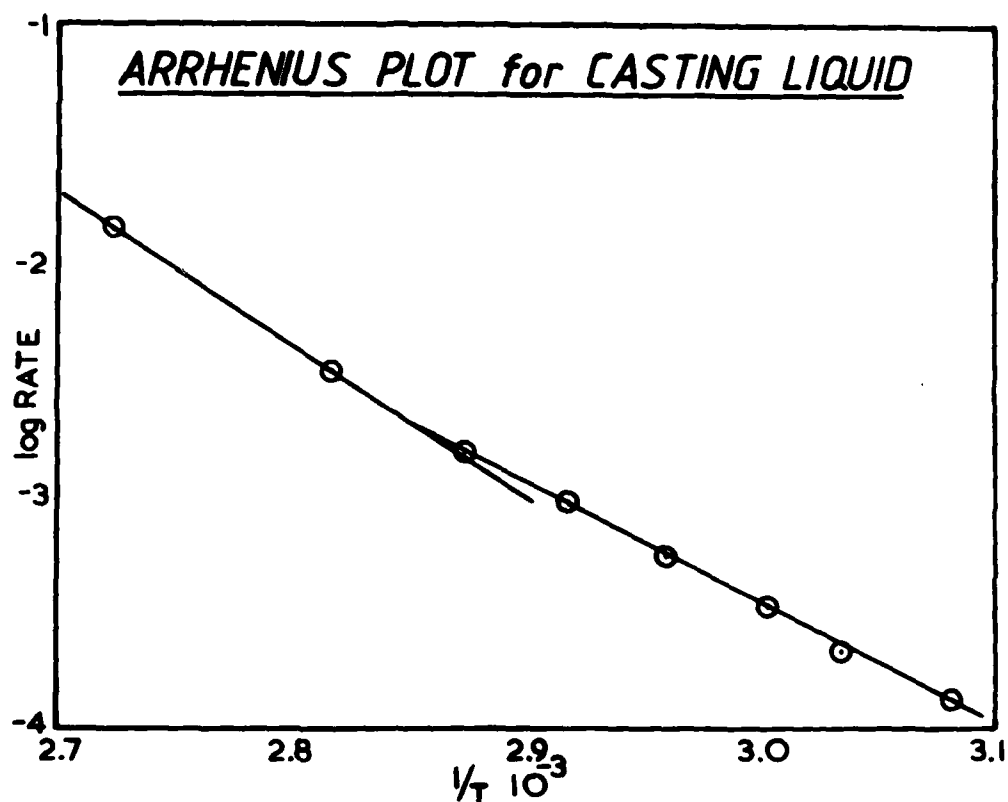


Fig 10

The feature most worthy of note from the experiment is that up to  $82^\circ\text{C}$  the only oxide of nitrogen observed was nitric oxide while at  $95^\circ\text{C}$  where a large proportion ca (80%) was nitrogen dioxide. This may indicate some change in the mechanism of the reactions controlling the oxidation and reduction of nitrogen oxides if not a change in the mode of nitric ester decomposition.

#### 10 CONCLUSIONS

The present study has been carried out over a period of a few months and consequently most of the experiments have been of an exploratory nature. Very many more experiments will have to be carried out on a much wider range of materials before a complete assessment can be made of the technique.

The traditional stability and compatibility tests are unsatisfactory for a number of reasons. One is that the species determined can be unrepresentative of the decomposition process. Perhaps a more serious problem relates to their lack of sensitivity, this requires that tests are run for long periods at high temperatures. The use of high temperatures is in turn unsatisfactory since long extrapolations have to be made to assess the performance of the propellant under normal storage conditions.

The present work illustrates that the chemiluminescence method goes a long way towards overcoming these serious deficiencies. Test times of a few minutes are possible at temperatures of less than 60°C. The areas in which the method might have applications are summarised below.

- 1 In determining the intrinsic decomposition characteristics of the material under test; ie stability.
- 2 In examining combinations of materials for increased decomposition rates; ie compatibility.
- 3 In determining the effect of propellant constituents on decomposition rates.
- 4 To examine the kinetics and mechanism of the decomposition process with particular reference to the effect of temperature.

## REPORT DOCUMENTATION PAGE

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Abstract A chemiluminescence NO <sub>x</sub> analyser has been used to study nitrogen oxides evolution from single-base and double-base propellants as well as from their nitrate ester ingredients. The technique has illustrated the importance of total oxides of nitrogen as a means of determining the rate at which these materials decompose. The potential of the method as a rapid and unambiguous means of assessing factors such as stability and compatibility is shown. The high sensitivity of chemiluminescence has also permitted the examination of the effect of temperature on decomposition rate down to ambient levels. Consequently one is able to identify changes in the decomposition mechanism as one goes from normal storage temperatures to elevated test temperatures.			